DYNAMIC INTERACTION OF TRACE GASES (VOCs, O_3, NO_x AND CO) IN SUBURBAN ATMOSPHERE OF SUB-TROPICAL INDIA

A

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INTRODUCTION

The increase of industrial activity, vehicular traffic and agricultural activities over the last century has resulted in a strong increase of emissions of volatile organic compounds (VOCs), carbon monoxide (CO) and nitrogen oxides (NO_X). VOCs and NO_x are the major precursors of ozone (O_3) and play an important role in tropospheric chemistry. The photochemical reactions of VOCs not only dominate the process of photochemical smog but also play an important role in the formation of urban haze (Xu et al., 2017). VOCs are defined as compounds with vapor pressure greater than 0.27 kPa (2 mm Hg) at room temperature (Wang et al., 2002). VOCs are gaseous non-methane organic compounds (NMOCs) with carbon atoms C_2 to C_{12} (Nguyen, 2009) such as aromatic hydrocarbons (Benzene, toluene, ethylbenzene, m/p-xylene, o-xylene [BTEX], naphthalene), aliphatic hydrocarbons (ethane, propane, n-hexane, 1,3-butadiene), terpenes, isoprene, monoterpene and sesquiterpene organic acids (acetic acid, formic acid), ketones (acetone, cyclohexanone), aldehydes (formaldehyde, acetaldehyde, benzaldehyde, butanal), alcohols (2-propanol, menthol, ethanol, 1- butanol) and others (Chatani et al., 2015). VOCs can be classified into three groups in terms of volatility: (i) very volatile organic compounds with a boiling point (BP) ranging from 0°C to 100°C, (ii) volatile organic compounds with a boiling point (BP) value of 100–260°C and (iii) semi-volatile organic compounds with a BP value of 260–500°C. Globally, VOCs are emitted from both biogenic and anthropogenic sources range from about 1200 to 1600 TgC/yr where biogenic emissions are highly dominant over anthropogenic emissions (Zhao et al., 2017).

After VOCs are discharged into the atmosphere, they not only cause pollution on local scale, but also play an important role on regional scale like photochemical ozone formation introduced by the reaction with hydroxy radicals (OH) in the troposphere in the presence of NO_x and sunlight (Pinto et al., 2007).

$$\mathbf{VOC + NO_X + sunlight \longrightarrow O_3 + \text{“other products”}}$$

The reaction of VOCs with (OH) and/or nitrate (NO_3) radicals serves as the dominant degradation processes for aromatic VOCs in the atmosphere and the resulting products contribute to secondary organic aerosol (SOA) formation by nucleation and condensation (Pitts and Pitts, 2000). The reaction

of toluene with NOx in the presence of a light source formed SOA with a significant aerosol yield and therefore, aromatic VOCs influence gas phase pollutants directly and particle-phase pollutants indirectly (Masih et al., 2016). In addition, both O_3 and SOA are radiatively active constituents of the troposphere and contribute to the climate change (Solomon et al., 2007). The effects of VOCs are not limited to climate, they also affect the animal and plants life. A number of epidemiological studies have reported the incidences of detrimental impacts on public health due to their toxicity, mutagenicity and carcinogenicity (Tyagi et al., 2016; Tuet et al., 2017). VOCs are hazardous air pollutants that cause or may cause cancer and other serious impacts upon human health, such as reproductive effects or birth defects, or adverse environmental and ecological effects.

In the lower atmosphere,VOCs are highly reactive and play an important role in the photochemistry, and acts as a sink of oxidants (such as O_3, OH and NO_X). Tropospheric ozone is a secondary pollutant that is formed in the troposphere from a complex series of sunlight driven reactions between NO_X, CO, and NHMCs and it is also transported into the troposphere from the stratosphere (Kumari et al., 2018). Ground-level ozone is formed from complex photochemical reactions of precursor VOCs, CO and NO_X.

CO serves to produce ozone and affects global ozone concentrations by its effect on OH and HO_2 radical concentrations. In troposphere OH radicals oxidize by CO to form peroxy ($HO_2^{\cdot}$**)** radicals which are involved in O_3 formation (Atkinson, 2000). Within the atmosphere, the major CO source is oxidation of methane by OH, producing formaldehyde (HCHO) and then CO. The tropospheric abundances of CO and CH_4 thus become important indices of the tropospheric oxidizing capacity, represented most specially by the concentrations of ozone and hydroxyl free radicals **(**Wang et al., 2002**).** On the other hand an important sink for HCHO, which, depending on the wavelength, yields H atoms and HCO radicals or hydrogen and carbon monoxide (Bauri et al., 2016).

$$\mathbf{HCHO + h\nu\ (325\ nm) \longrightarrow H + HCO}$$

$$\mathbf{HCHO + h\nu\ (325\ nm < \lambda < 360\ nm) \longrightarrow H_2 + CO}$$

Formaldehyde is also linked with the so called odd hydrogen family (OH, HO, H) by the following reactions:

$$HCO + O_2 \longrightarrow HO_2 + CO$$

$$CO + OH + M \longrightarrow H + CO_2 + M$$

$$H + O_2 + M \longrightarrow HO_2 + M$$

With regard to these reactions, formaldehyde has to be considered as a significant radical source.

Nitrogen oxides (NO and NO_2) play an important role in ground-level O_3 concentrations (Lal et al., 2000). Greater NO_2 concentrations give rise to O_3 levels due to its photolysis, while NO serves as the major source for the production of NO_2 as it is oxidized in the presence of sunlight and VOCs (Kumar et al., 2017). The oxides of nitrogen, NOx (NO + NO_2) are mainly emitted in the atmosphere as NO, which is subsequently transformed into NO_2 and other nitrogenous species. Nitrogen oxides play a central role in photochemical production of ozone in the troposphere. The dominant source of NO_x in the atmosphere is fossil fuel combustion, biomass burning, emission from soil and by lightning activity (Tyagi at et., 2016). The NO_2 formation in urban atmospheres is mainly due to the NO oxidation by HO_2 radical produced by photo oxidation of NMHCs. The main chemical sink of NO_2 is highly water soluble a photo chemically relatively long-lived nitric acid (HNO_3).

VOCs and NO_x mainly emitted from natural sources, like volcanoes, vegetation, ocean and forest fires. Anthropogenic activities have become important sources of VOC and NO_X emissions into the atmosphere, so that they account for 25% of VOCs in global atmosphere (Montero et al., 2018).

The predominant anthropogenic sources of VOCs are emissions from gasoline, diesel, and liquefied petroleum gas (LPG), fuel evaporation, petroleum distillation, oil refineries, emissions from industries such as shoe making, furniture manufacturing, solvents in paints and consumer products, coal and biomass burning (Bari et al., 2018).

Vegetation is the most abundant natural source of VOCs. It is an important primary source of acetone and probably also of certain other carbonyls (Singh et al., 2016). Ocean is the main source of propanal and acetaldehyde in the atmosphere. Release to the atmosphere occurs because VOCs present in the oil cells of plants are exuded as vapor into surrounding epithelial cells or intercellular spaces and reach the leaf surface through mesophyll and epidermal cells or through cuticles (Yokouchi

et al., 1985). The types of hydrocarbon emitted by vegetation depend on the composition within the oil cell and may differ according to the plant family. Ethene is plant hormone and is emitted by plants, soil, oceans. The emission rate of each component is determined by the product of its concentration in the oil cell and the saturated vapor pressure. Since saturated vapor pressures follow a log-linear relationship with temperature, strong diurnal and seasonal variations in the flux of VOCs in the atmosphere are observed. Isoprene, terpenes, alcohols, carbonyl compounds and esters are the major components released by plant emission. Some of these can actively participate in photochemical smog pollution, being extremely reactive with OH radicals and ozone (Graedel et al., 2012). Annual global VOCs flux from plants has been estimated to be 1150 Tg-C/yr consisting of 44% isoprene, 11% monoterpenes, 22.5% other reactive hydrocarbons and 22.5% other non-reactive hydrocarbons (Kansal et al., 2009). Photochemical reaction of isoprene in the lower atmosphere, especially in polluted urban areas, can contribute a significant amount of ozone to the ambient air. Temperature and light intensity are the most important factors controlling biogenic emissions of isoprene (Xiaoshan et al., 2000). Globally, the largest sources of VOCs are tropical and extra-tropical forests, which emit VOCs (like isoprene, α - and β-pinene and methanol) in large quantities (Guenther et al., 2012).

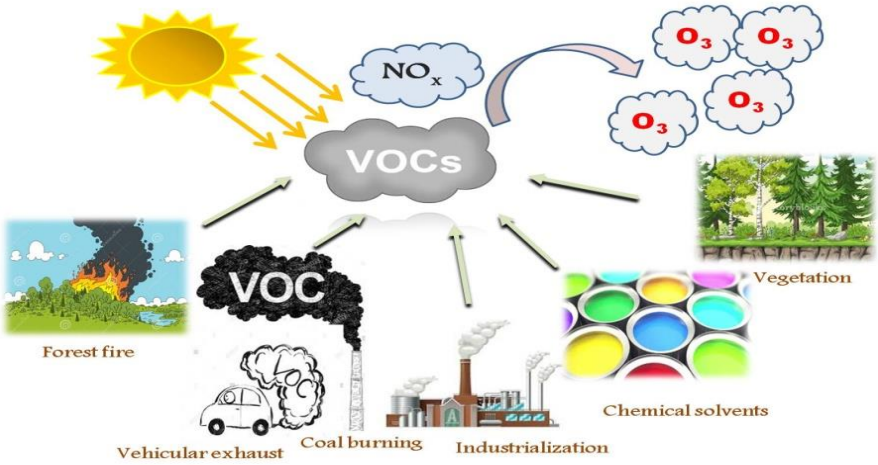


Figure 1: Sources of VOCs

After being emitted into atmosphere, VOCs undergo four main processes: dispersion, transformation, chemical reactions and deposition. Dispersion provides transportation and dilution by distributing the VOCs over different air parcels of the atmospheric boundary layer. Physical

transformation includes condensation of gaseous VOCs into organic particles, adsorption on their surface or solution in water droplets. Chemical reactions convert VOCs into organic or inorganic molecules, which in turn undergoes dispersion and transformation processes. Deposition includes wet and dry deposition of VOCs into the water and soil reservoirs by sedimentation or scavenging processes (Chauhan et al., 2014).

Increase in the anthropogenic activities resulted in increase in tropospheric ozone concentrations observed over the past century. Ground-level ozone is formed from complex photochemical reactions of precursor VOCs and NO_X (Tiwari et al., 2010). Formation of tropospheric ozone is initiated by the reaction of various VOC or CO with the $OH^{\cdot}$ radical, followed by the conversion of NO to NO_2 with the reaction intermediate (HO_2) or (RO_2) radicals, which also regenerates $OH^{\cdot}$. NO_2 is photolyzed to generate atomic oxygen, which combines with O_2 to create O_3.

The photochemical oxidation of VOCs initiated by rapid reaction with ($OH^{\cdot}$) involves various chemical chain reactions and several gaseous intermediates such as ($RO_2^{\cdot}$), (HO_2), peroxy acetyl nitrate (PAN), carbonyls and organic nitrate compounds ($RONO_2$).

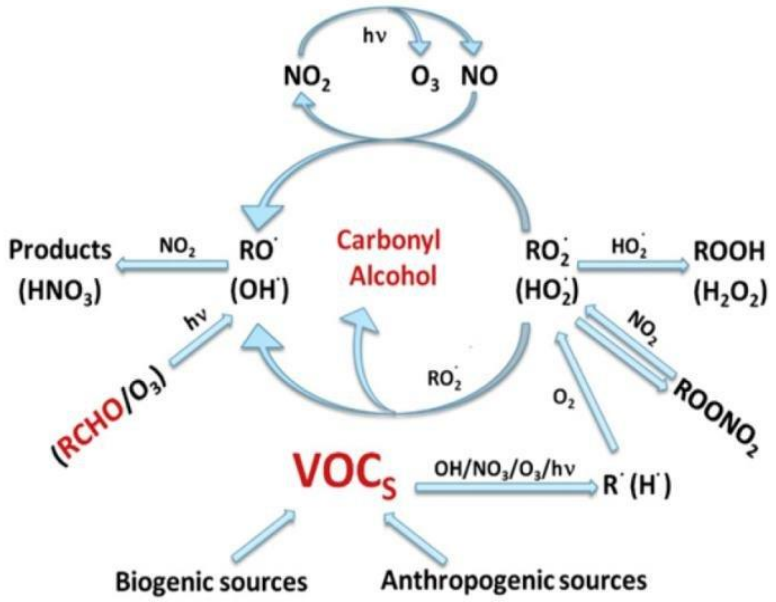


Figure 2: Tropospheric ozone formation

The essential role played by VOC is the oxidation of NO, emitted by combustion process to NO_2 (Pitts and Pitts, 2000). Which lead to the conversion of NO to NO_2, and hence, promotes O_3 accumulation and the efficient regeneration of the OH· (Seinfeld and Pandis, 2006). The NO_2 formation in urban atmospheres is mainly due to the NO oxidation by peroxy radicals produced by photooxidation of nonmethane hydrocarbons (NMHC). The main chemical sink of NO_2 is highly water soluble a photochemically relatively long-lived nitric acid (HNO_3).

$$\mathbf{NO_2 + OH\ (+M) \longrightarrow HNO_3\ (+M)}$$

HETEROGENEOUS REACTION OF VOCs

Isoprene, with an annual global flux of 440-660 TgC, accounting for ~50% VOCs, is one of the most important VOCs in the atmosphere (Guenther et al., 2012). Few studies have focused on the heterogeneous fate of isoprene, probably due to its extraordinarily high volatility and less reactive carbon group (e.g., C=C bond) towards particle surfaces. However, Limbeck et al, (2003) found that heterogeneous reaction of isoprene on sulphuric acid could produce macromolecular "humic-like substances" (HULIS) and thus contribute to SOA formation. In contrast, Connelly and Tolbert, (2010) suggested that this heterogeneous reaction could not significantly contribute to SOA, but, rather, its products (monoterpenes and cyclic sesquiterpenes) may influence the nucleation and growth of ultrafine particles. These studies demonstrate that heterogeneous chemistry of isoprene may also play an as yet unclear but potentially important role in the atmosphere.

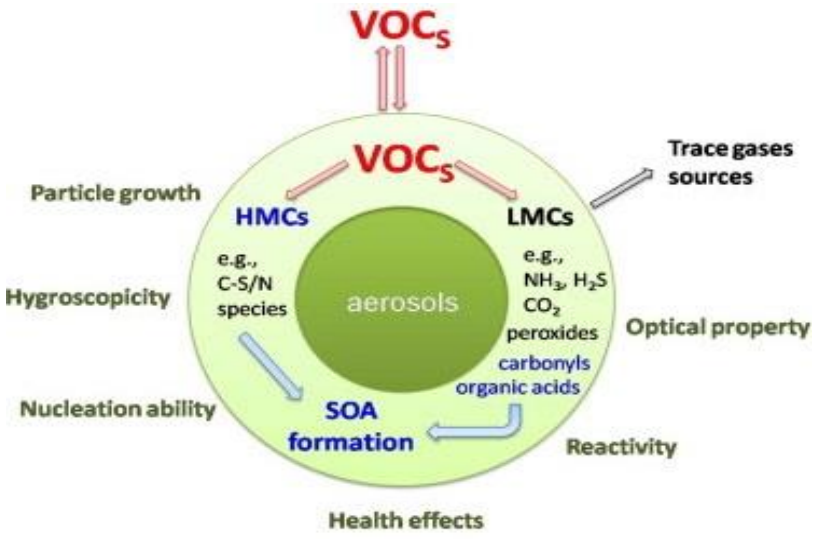


Figure 3: Heterogeneous reactions of VOCs

Formaldehyde (HCHO), the smallest and most abundant aldehyde, is one of the most important carbonyl compounds (Vrekoussis et al., 2010). HCHO can contribute to the formation of HO_2· radicals and peroxyacyl nitrates and thus its percentage may strongly impact the photochemical oxidant cycle. Therefore, it is worth exploring the potential sink for HCHO via its heterogeneous reaction pathways. Heterogeneous reactions of HCHO on mineral dust model compounds, including SiO_2 (Carlos-Cuellar et al., 2003), a-Al_2O_3 (Xu et al., 2017), a-Fe_2O_3 (Carlos-Cuellar et al., 2003), and TiO_2 (Sassine et al., 2010) were investigated in laboratories using various techniques such as transmission-Fourier transform infrared (T-FTIR) spectrometry.

VOCs have adverse effects on plants can clearly be shown by the formation of photo oxidants and climate change effects (Pinto et al., 2010). Some experimental investigations indicate that ethene has direct phytotoxic effects on plants. Ethene is of special interest, because it is produced by many plants as a phyto-hormone influencing a variety of physiological processes, such as growth, differentiation and senescence, one of its best-known effects is the stimulation of fruit ripening (Dudareva et al., 2006). However, various stresses (e.g. drought, flooding, wounding, pathogens and gaseous air pollutants) enhance the biosynthesis of ethene, which acts to intensify the stress. Typical symptoms are epinasty of leaves, growth inhibition, internode shortening, abnormal bud withering, premature discoloration and yellowing of leaves, senescence and abscission of flowers, chlorosis and necrosis (Pinto et al., 2010).

Apart from atmospheric chemistry, VOCs have a significant role in human health (Lal et al., 2008).VOCs can enter the body easily through the air and therefore, cause health risk on long time exposure even to low concentrations affecting different target organs e.g. central nervous system, respiratory system, liver, kidney, reproductive system, etc. (Buczynska et al., 2009). The effects could be ranging from non-carcinogenic to carcinogenic effects. Many VOCs are toxic, and among them, some are suspected to be carcinogenic (Civan et al. 2012). Carcinogenic effects are characterized by lung, blood (leukaemia and non-Hodgkin lymphoma), liver, kidney and biliary tract cancer (WHO, 2000). The International Agency for Research on Cancer (IARC) classified benzene as a potential

carcinogenic type I (IARC 2006). It produces central nervous system toxicity and feto-toxicity (Fustinoni et al., 2000).

LITERATURE REVIEW

Worldwide rapid urbanization and industrialization during the recent decades, have introduced many chemicals into the environment which lead to deterioration of environment quality (Srivastava et al., 2011). Air pollutants like particulate matter (PM), oxides of nitrogen (NO_x), carbon monoxide (CO), sulphur dioxide (SO_2) and volatile organic compounds (VOCs) pose a serious health hazard and concern for agriculture and global climate (Gaur et al., 2016) .

VOCs are introduced into the atmosphere through anthropogenic activities and biogenic sources (Atkinson, 2000; Kumar et al., 2018). Many VOCs have been reported to be toxic, carcinogenic or mutagenic. High levels of VOCs have been observed in Asian countries (Srivastava et al., 2005). The levels of VOCs have been reported at various countries including India at different sites such as rural, urban, industries and mountains.

VOCs LEVELS AT DIFFERENT SITES IN INDIA

India is the second largest contributor to the emission of non-methane VOCs (Kurokawa et al., 2013).

Table-1: VOCs, NO_x, O_3 and CO levels reported in different sites of India

Site	Sources	Sampling Method	Analysis	Pollutants and Concentrations					Reference
				VOCs (µg/m^3)		O_3 ppb	NO_x ppb	CO ppb	
Southern Himalayan	Forest fires, bio fuel and agricultural crop residue burning	Canister method	GC-MS	Ethane	20.9	54.1	13.6	284	**Kumar et al., 2019**
				Formaldehyde	42.7				
				Acetaldehyde	42.2				
				Benzene	8.1				
				Menthol	55.0				
				Toluene	5.7				
				Xylene	0.9				
				Isoprene	4.7				
				Terpenes	3.0				
				Pentane	0.9				
Agra	Vehicular emission	Activated charcoal tube	GC-FID	Benzene	39.7	45	20.6	523	**Verma et al., 2017**
				Toluene	45.5				
				Ethylbenzene	5.5				
				m/ p- Xylene	5.1				

				o- Xylene	4.3				
Dehradun	Vehicular exhaust, gasoline evaporation, solvent usage	Activated charcoal tube	GC-FID	Benzene	19.8	-	-	-	**Bauri et al., 2016**
				Toluene	76.2				
				Ethylbenzene	7.7				
				m/p-Xylene	16.4				
				o-Xylene	11.7				
Delhi	Traffic emissions, solvent usage and industrial emissions	Activated charcoal tube	GC-FID	Styrene	4.2	17.6	15.9	1900	**Singh et al., 2016**
				Chloroform	1.6				
				Carbon-tetra Chloride	1.5				
				Benzene	8.4				
				Toluene	24.8				
				Ethylbenzene	5.7				
				m/p-xylene	25.2				
				o-xylene	15.3				
Bhubaneswar	LPG emissions and biomass burning	Activated charcoal tube	TD-GC-FID	Ethane	0.3	65	-	1900	**Panda et al., 2015**
				Ethylene	0.1				
				Propane	2.8				
				i-Pentane	1.4				
				n-Butane	0.6				
				Acetylene	0.2				
				n-Pentane	2.5				
				Propylene	0.4				
Ahmedabad	Vehicular emission, biomass burning	PFA Teflon tube	TD-GC-FID	Methanol	22.0	20.7	9.5	-	**Sahu et al., 2015**
				Acetonitrile	0.9				
				Acetone	6.1				
				Isoprene	1.6				
				Benzene	2.6				
				Toluene	7.3				
Hyderabad	Vehicular exhaust, gasoline evaporation, solvent usage	Canister method	GC-FID	Ethylene	3.1	55	5.3	-	**Swamy et al., 2012**
				Acetylene	2.62				
				Ethane	28.5				
				Propane	3.5				
				n- Butane	2.5				
				i-Pentane	7.8				
				n-Pentane	116.7				
				Toluene	8.1				
				o/m- Xylene	2.1				
				p- Xylene	5.1				
Aurangabad	Vehicular emission and industries emission	Canister method	GC-FID	Ethylene	0.5	67	-	270	**Lal et al., 2008**
				Acetylene	0.1				
				Ethane	1.7				
				Propane	0.2				
				n- Butane	0.5				

				Ethylene	0.6				
Kolkata	Combustion of fossil fuels and small industries	Activated charcoal tube	GC-FID	Formaldehyde	27.8	-	-	-	**Majumdar et al., 2008**
				Acetaldehyde	18.3				
				Acetone	12.2				
				Benzene	137.5				
				Toluene	643.6				
				m/p- Xylene	209.7				
				o- Xylene	68.2				
				Ethylbenzene	118.0				
Mumbai	Industrial, Traffic intersection and combustion of fossil fuels	Activated charcoal tube	GC-MS	Benzene	127.2	-	-	-	**Srivastava et al., 2006**
				Toluene	128.7				
				Ethylbenzene	0.29				
				m-Xylene	0.16				
				Carbon-tetra chloride	0.54				

Non-methane hydrocarbons (NMHCs), CO, NO_x and O_3 have been reported at high altitude site of southern Himalayas (29.4 °N, 79.5 23 °E, 1958 m amsl) during forest fires (Kumar et al., 2019). Mean of VOCs emissions was 0.20 Tg. Incomplete combustion was considered as the important cause of VOCs emissions during forest fires. Similarly, 1.1 Tg of VOCs reported during April through October (1998) at boreal forest fires in Siberia (Kajii et al., 2002). Peak emission (~3.093 Tg) of NMVOCs were also reported during the peak forest fire episode of Indonesia in 2015 (Pribadi et al., 2017). Average ozone levels were observed higher during April 2016 (54.1 ppb).

Singh et al, (2016) reported the concentration of VOCs, NO_x, CO and O_3 at Delhi. Sampling of VOCs was carried out by activated charcoal tube analyzed by GC-FID. The mean concentration of VOCs were 160.15 μg /m^3). Toluene was the most abundant followed by the xylene and benzene. The average concentration of O_3 and NO_x were observed 17.6 and 15.9 ppb, mean levels of CO were observed to be 1.9 ppm.

Sahu et al, (2015) reported the concentration of VOCs at road junction in Ahmedabad. Perfluoroalkoxy (PFA) teflon tubes were used for sample collection and analysed by Thermal Desorption-Gas Chromatography-Flame Ionization Detector (TD-GC-FID) technique. Diurnal trend of VOCs was also measured Proton-Transfer-Reaction Time Of Flight Mass Spectrometer (PTR-TOF-MS), showed higher concentration in morning and evening. NO_x and CO are the main precursors of

O_3, and followed a reverse diurnal pattern, lowest concentration of NO_x and CO was observed during afternoon hours when O_3 showed highest concrntration during afternoon (Beig et al., 2007).

Swamy et al, (2012) observed variation in VOCs, NO_x, CO and O_3 during weekends and weekdays at Hyderabad. The high O_3 levels on weekends were attributed to low levels of NO_x and CO as compared to weekdays, therefore loss of ozone through titration and heterogeneous reactions were low. In addition, during weekends ozone formation was VOC sensitive, therefore high VOC/ NO_x ratio resulted in high levels of ozone. At a semi-urban site of Dibrugarh, Bhuyan et al. (2014) observed the maximum ozone in premonsoon season and that of CO and NO_x was seen maximum in the winter season.

Majumdar et al, (2008) in Kolkata concluded from his study that vehicular emissions were the dominant source, which contributed 38.8% to 44.8% toward the TVOCs level. Srivastava and Majumdar, (2011) identified the major sources of VOCs in four metro cities of India - Delhi, Mumbai, Chennai, and Kolkata and reported highest evaporative emissions in Delhi followed by Mumbai, and Kolkata. They concluded that vehicular emissions were the major contributors followed by other activities like paints, newspaper printing, computer printers, graphic art applications and consumer products.

Lal et al, (2008) reported the levels of VOCs, O_3 and CO at Aurangabad. The average mixing ratios of O_3, which were in the range of 60–90 ppbv, are significantly higher compared to the typical values reported for urban sites of India. However, levels of primary pollutants e.g., VOCs, CO, etc. at these sites were much lower than urban sites, but higher compared to previously observed values surrounding marine region of India. The estimated ratios of NMHCs and CO indicate fossil fuel combustion process as the dominant sources.

Ambient VOCs levels in Dehradun were reported by the Bauri et al, (2016). Among BTEX, toluene was found to be the most abundant monoaromatic species in the ambient atmosphere of Dehradun. Similar trend has also been observed by researchers in other areas like Turkey (Muezzinoglu et al., 2001); Algiers (Kerbachi et al., 2006); Rio de janeiro (Martins et al., 2007); Delhi (Hoque et al., 2008); in Kolkata (Majumdar et al., 2011); Mumbai (Pandit et al., 2011); Chennai (Mohan and Ethirajan, 2012). Among BTEX, the mean concentration of toluene was followed by

benzene, m, p-xylene, o-xylene and ethylbenzene successively in three seasons for all the sites. Toluene at Malsi was highest in summer (118.3±39.3μg/m³,) followed by winter (193.8±54.6 μg/m³) and monsoon (134.6±36.3 μg/m³).

BTEX concentration at suburban site of Agra reported by Verma et al, (2017). Activated charcoal method use for sampling and analyzed compounds using GC-FID. Their study reported that toluene showed the maximum average concentration (45.5±25.4 μg m^3) followed by benzene, ethyl-benzene, m, p-xylene and o-xylene. Higher concentration of O_3 and NO_x was observed in winter season due to increased anthropogenic activities. Higher BTEX levels were attributed to various emission sources such as biomass burning, vehicular emission, open burning of crop residue; these facts were directly related to the influence of the distance of source emission (dilution and photochemical activity) (Chan et al., 2003). Similar trend has also been observed by Srivastava et al., 2006; Hoque et al., 2008; Singh et al., 2012.

Table-2: VOCs, NO_X, O_3 and CO levels reported in different countries

Site	**Sources**	**Sampling Method**	**Analysis**	**Pollutants and Concentrations**					**Reference**
				VOCs (μg/m^3)		**O_3 ppb**	**NOx ppb**	**CO ppb**	
Xi'an (China)	Industrial emission	Canister method	GC-MSD-FID	Isoprene	0.84	55.4	13.2	-	**Sun et al., 2019**
				n-Butane	1.71				
				Propylene	0.34				
				Cyclopentane	0.06				
				n- Hexane	0.97				
				Ethylene	2.18				
				Alkyne	3.79				
				n- Heptane	0.19				
				Propane	1.50				
				n- Pentane	0.60				
				Benzene	1.7				
Logan (Utah)	Coal burning, photochemical industries	Canister method	GC-FID	Toluene	4.5	22.7	5.7	-	**Mukerjee et al., 2019**
				Ethylbenzene	0.8				
				m,p-Xylene	2.6				
				Benzene	2.2				

Ulsan (South Korea)	Industrial and urban	Passive air sampling	GC-MS	Toluene	8.4	-	-	-	**Kim et al., 2019**
				m/p-Xylene	3.0				
				o-Xylene	2.7				
				Ethylbenzene	3.2				
				Cyclohexane	0.2 ± 0.1				
				n-Butane	2.9 ± 3.3				
Alberta (Canada)	Oil sands communities	Canister method	GC-MS	Isobutane	1.3 ± 1.3	-	-	-	**Bari et al., 2018**
				Acetone	6.7 ± 5.1				
				α- Pinene	1.3 ± 1.9				
				Isopentane	2.4 ± 2.9				
				Isoprene	2.6 ± 2.5				
				Acetaldehyde	8.5 ± 6.4				
				Propane	5.4				
Wuhan (China)	Vehicular exhaust, coal burning, solvent usage and biomass burning	TH-300B monitoring system	GC-FID-MS	Ethane	4.2	34.3	17.4	-	**Hui et al., 2018**
				Acetone	2.2				
				Isobutane	1.1				
				Propene	0.6				
				Isobutene	0.3				
				Chloro-methane	0.3				
				n-Hexanal	1.8				
				Acetylene	2.3				
				Ethene	2.7				
				Ethane	1.6 ± 0.5				
Hanoi Vietnam	Fossil fuel, Vehicular emission	Sorbant tubes	TD-GC-FID	Propane	2.4 ± 2.8	25.7	18.1	900	**Sakamoto et al., 2017**
				n-Butane	2.3 ± 2.8				
				Ethylene	1.8 ± 1.1				
				Isoprene,	0.8 ± 0.7				
				i-Pentane	5.6 ± 4.9				
				Benzene	2.3 ± 1.3				
				Toluene	4.8 ± 3.7				
				Ethylbenzene	0.7 ± 0.4				
				Xylene	0.5 ± 0.4				

				Styrene	0.2 ± 0.1				
				Benzene	0.7				
Ottawa Canada	Industrial and Vehicular emission	Activated charcoal tube	GC-FID	Toluene	2.4	25	8.01	-	**Oiamo et al., 2015**
				m/p-Xylene	1.0				
				Ethane	0.08				
Guangzhou China	Vehicular emission and fossil fuel	Canister method	TD-GC-FID	Propane	0.09	29.6	18.1	-	**Zou et al., 2015**
				n-Butane	0.06				
				Ethylene	0.04				
				Isoprene,	0.07				
				Benzene	0.06				
				Toluene	0.05				
				Ethylbenzene	0.04				
				Styrene	0.04				
				Xylene	0.03				
				Benzene	1.7				
Aliaga (Turkey)	Industrial emission, petroleum refinery and photochemical complex	Passive sampling	TD-GC-FID	Hexana	0.8	48	15	-	**Civan et al., 2015**
				Toluene	1.5				
				n-Octane	0.5				
				Styrene	1.0				
				Ethylbenzene	0.3				
				n-Nonane	1.2				
				o-Xylene	0.2				
				m/p-Xylene	0.6				
				Styrene	0.6				
Izmir (Turkey)	Industrial plant and vegetation	Passive sampler	GC-MS	Isopropyl benzene	1.9	-	-	-	**Dumanoglu et al., 2014**
				Isopentene	8.1				
				n- pentane	26.9				
				Carbon tetra chloride	0.6				
				Chloro-benzene	0.04				
				Chloroform	0.4				
				Ethane	7.1				
London (UK)	Fuel evaporation, biomass burning and LPG usage	Canister method	GC-FID	Propane	2.7	-	-	**530**	**Von Schneidemesser et al., 2010**
				n-Butane	2.0				
				Ethylene	1.3				
				n-Pentane	0.6				
				Benzene	0.4				
				Toluene	1.0				
				Ethylbenzene	0.1				

				o-Xylene	0.2				
				Ethane	2.5±1.1				
Yokohama (Japan)	Industrial sources and gasoline Use	10-L Flek polyester bags.	GC-FID	Propane	5.5±5.7	-	-	-	**Tiwari et al., 2010**
				Isobutane	2.1±1.1				
				Ethylene	3.9±3.4				
				Acetylene	1.5±1.4				
				Propylene	0.8±0.6				
				Benzene	0.7±0.4				
				Toluene	3.1±1.7				
				Ethyl benzene	0.8±0.6				
				Xylene	0.8±0.5				

Sun et al, (2019) reported the VOCs, NO_x and O_3 at Xi'an, China. They reported diurnal variation, highest concentration was observed in the morning (49.6 ± 40.1 ppbv) and the lowest VOCs concentration in the night (28.4 ± 25.6 ppbv) which may be due to the lowest anthropogenic activity level (Li et al., 2017). O_3 was the major pollutant during the sampling period with average concentration of 55.4 ppb, and even exceeded the national standard in afternoon period. NO_2 concentration showed diurnal variations with significant low peak during the afternoon period.

Mukerjee et al, (2019) reported levels of VOCs, NO_x and O_3 at Logan, Utah. Among BTEX toluene was found to be the most abundant monoaromatic species in the ambient atmosphere of Utah. Averages for NO_x showed a sharp increase during morning hours followed by a sharp decline to early afternoon. Average O_3 levels increased from approximately 12 PM – 4 PM. This is consistent with the formation of daytime O_3 from elevated morning levels of nitrogen oxides and other precursors.

Kim et al, (2019) reported the concentration of VOCs at industrial and urban site at (Ulsan) South Korea, during summer, fall, winter and spring. The average concentration of total VOCs was the highest in spring, followed by fall, summer and winter. Toluene was showed highest mean concentration followed by ethylbenzene , m,p-xylenes, o-xylene, and benzene.

Hui et al, (2018) reported VOCs concentration and trace gases at urban region of Wuhan. The results revealed that the annual average concentration of total VOCs was 34.65 ppbv. Alkanes were the species with the largest concentration, which accounted for 45.88% of TVOCs, and propane, ethane and ethylene were the most abundant components. Vehicular exhaust (24.42%), industrial sources (16.43%), coal burning (14.18%), solvent usage in painting/coating (13.48%), liquefied

petroleum gas (LPG) usage (12.57%), fuel evaporation (11.34%), biomass burning (5.11%) and biogenic sources (2.47%) were main sources of VOCs identified by positive matrix factorization (PMF). Alkenes contributed the most to O_3 formation, which accounted for 48.34%. The ozone weekend effect refers to the increase in ozone concentration, and the decrease in the concentration of ozone precursors such as CO, NO, NO_2, NO_x and VOCs on weekends as compared to weekdays (Wang et al., 2016). Similar trend of VOCs has also been observed in China by Zou et al, (2015).

Sakamoto et al, (2017) reported the 1-week observation of VOCs in September 2015 and a year-long campaign measurement of O_3, NO_x and CO between October 2015 and December 2016 at inner city area of Hunoi. Overall mean values of O_3, CO and NO_2 mixing ratios were 19.3 ± 15.3 ppb, 1.3 ± 0.8 ppm and 21.4 ± 11.8 ppb, respectively. The most abundant species were i-pentane and toluene, which were observed at 5.6 and 4.8 ppb, respectively.

Tiwari et al, (2010) reported the levels of VOCs observed at Yokohama, Japan. Among BTEX the mean concentration of toluene was highest followed by ethylbenzene, benzene and xylene. High concentration of toluene at industrial location justified by the petrochemical industrial activities at this site. The petrochemical industries at this location include industries such as petrochemical refining and storage, polypropylene, paints, solvent, and varnish. The high concentration of toluene was also reported in several studied like Turkey (Muezzioglu et al., 2001); in China (Wang et al., 2002); in Algiers (Martins et al., 2007).

The benzene series are important components of VOCs, which can be used to determine the source information of pollutants by the ratio of toluene to benzene (T/B) (Yang et al., 2016). T/B < 2 indicates that the pollutants in the area are significantly affected by vehicle exhaust emissions and the larger the value of T/B, the smaller the impact of vehicles and the greater the impact of other VOC sources (Chen et al., 2012). T/B > 2 indicates that there are other sources besides vehicle exhaust emissions, and when T/B reaches 10 or higher, this indicates that there are strong industrial emission sources nearby (Kumar et al., 2018).

Acetylene is often used as a tracer for combustion sources (Barletta et al., 2005). The ratios of various hydrocarbon species to acetylene are commonly used to identify the contributions of other sources to combustion sources and the ratios of propane, n-butane and isobutane to acetylene are

commonly used to identify the contributions of pollutants from LPG leakage (An et al., 2014).The ratios of benzene, toluene, and C_8 and C_9 aromatics to acetylene are often used to determine the contributions of pollutants from the volatilization of industrial coatings, the usage of solvents and the volatile emissions from the production process of industries (Zhang et al., 2012).

SEASONAL AND DIURNAL VARIATION

VOCs, NO_x and CO showed a distinctive seasonal variation with higher value in winter and lower during summer and autumn (Kumar et al., 2017; Hui et al., 2018). The concentration of O_3 was found to be highest in summer followed by winter and autumn. Higher solar radiation and temperature during summer result in more photochemical ozone production. Lower O_3 levels were recorded in winter which could be attributed to the shorter daylight hours (Wang et al. 2013). Variation in VOCs, NO_x and CO concentrations in the atmosphere is mainly influenced by the changes in their sources, OH radicals and atmospheric mixed states (Zhu et al., 2014). Normally, the high temperature, strong solar radiation and strong atmospheric convection lead to atmospheric photochemical reactions being more active and then, the photochemical depletion of VOCs, NO_x and CO is accelerated and thus, that concentration of these pollutants were lower during summer. In contrast, the atmospheric boundary layer is lower during winter, and the temperature stratification is more stable than that during summer, which is not conducive to the dilution and diffusion of pollutants. The low temperature and wind speed suppressed the photochemical reactions, and reduced consumption of VOCs, and these factors lead to a generally high concentration of VOCs during winter. Halohydrocarbons mainly come from industrial processes, and thus, the change in pollution sources has a great influence on the concentration of halohydrocarbons. Unlike anthropogenic VOCs, isoprene levels were highest in summer and lowest in winter. Isoprene seasonal variation suggests that biogenic emission is influenced (i.e. enhanced in summer and inhibited in winter) to a greater extent by seasonal change than photochemical consumption and dispersion.

Oxygenated volatile organic compound (OVOCs) exhibited completely different seasonal variations from TVOC concentrations. The complex sources of atmospheric OVOCs, photochemical reaction processes, biological emissions and anthropogenic emission sources could all affect the

concentration changes in OVOCs. OVOCs are the products of atmospheric photochemical reactions, and the more active photochemical reactions, the more OVOCs are generated in the atmosphere. Therefore, less photochemical production of OVOCs during winter and more photochemical productions during summer and autumn were observed (Hui et al., 2018). The biological sources of OVOCs include live plant leaves and fruits (Laffineur et al., 2012) and the decomposition or decay of organic matter, such as plant litter (Gray et al., 2010). In addition, the decomposition and transfer of green wastes, vegetables, fruits and garbage can also have a certain effect on OVOC concentrations (Kumar et al., 2017). Similar seasonal variations of VOCs were reported at different sites such as Mumbai (Srivastva et al., 2006), Kolkata (Majumdar et al., 2008), Agra (Singla et al., 2012), Delhi (Singh et al., 2016); Kumar et al., 2017) and Dehradun (Bauri et al., 2018).

In order to understand the sources, transport, and chemical formation/destruction of the air pollutants, the study of diurnal variability of the pollutants are necessary. Factors such as human activities, nearby local traffic volume, and flow throughout the day and meteorological parameters explain the diurnal variability of the air pollutants (Olumayede et al., 2012). VOCs exhibited higher values in the morning (7:00–10:00) h and evening (16:00–19:00) h while lower values during daytime (10:00 to 16:00) h during all seasons (Singh et al., 2016; Kumar et al., 2017). The higher levels during morning/evening hours could be due to higher emissions from vehicles during peak traffic hours. In addition, the diurnal variation in VOCs showed obvious consistency with the variations in NO_x and CO, whereas the diurnal variation of O_3 was the opposite. VOCs, NO_x and CO showed a bimodal peak which showed higher concentration in late night and evening, O_3 showed unimodal peak and higher concentration in afternoon. O_3 levels start increasing after the sunrise coinciding with the increasing solar radiation and reach peak value around 14:00 to 15:00 h. Thereafter, it decreases gradually and reaches minimum values in the night due to absence of solar radiation (Hui et al., 2018).

VOCs are important precursors to O_3, which can be oxidized by OH radicals, NO_3 radicals and O_3. Among them, the reactions with OH radicals and O_3 are the main sedimentation reactions for VOCs during daytime, and the reactions with NO_3 radicals and O_3 are the most important chemical reactions occurring at night (Atkinson et al., 2003; Xu et al., 2017). However, the reaction rate of the NO_3 radical is much lower than that of the OH radical, and thus, the concentration of all VOC

components is higher at night (Xu et al., 2017). In general, halohydrocarbons, alkynes and short chain alkanes are low reactivity hydrocarbons, whereas long chain alkanes, alkenes, aromatics (except benzene) and OVOCs are active hydrocarbons (Zhang et al., 2007; Xu et al., 2017). For the active species, the photochemical reaction activities are relatively strong, whereas the high temperature and strong solar radiation at noon leads to the enhancement of photochemical reactions and the consumption of the active species; thus, the concentration gradually decreased. In addition, lower relative humidity is also conducive to photochemical reactions. At night, the decrease in OH radicals reduce photochemical reactions, and the sharp reduction in the height of the boundary layer; the significant decrease in wind speed and the increase in vehicle exhaust emissions result in an increase in the concentration of active species (Kumar et al., 2018). Similar diurnal pattern of VOCs have been reported by other studies (Tiwari et al., 2010; Yang et al., 2016; Bari et al., 2018; Kim et al., 2019).

OBJECTIVES

On the basis of above literature review it is evident that there have been no systematic and simultaneous measurements of VOCs specially for lower alkanes and hydrocarbons along with surface O_3, NO_x and CO in this region. Recognizing the importance of such studies, it is proposed to come out the simultaneous measurements of most prominent air pollutants like VOCs (alkanes, alkenes, aromatic hydrocarbons) along with O_3, NO_x and CO, with the following objectives:

- To study diurnal and seasonal variation of VOCs at Dayalbagh (suburban site) and comparison with few representative samples from traffic (NH-44, Bhagwan talkies) and rural site (Sikandarpur).
- To determine O_3 formation potential of VOCs.
- To study diurnal and seasonal variations of NO_x, CO and O_3.
- Identification of emission sources using Principal Component Analysis (PCA).
- Theoretical health risk assessment of VOCs.

METHODOLOGY

SITE DESCRIPTION

The sampling will be carried out at Dayalbagh Educational Institute (DEI), Dayalbagh (sub-urban site), Bhagwan talkies (traffic site) and Sikandarpur (rural site). DEI is surrounded by a small residential community and agricultural fields whereas Bhagwan talkies, (near National Highway-44. NH-44 commonly referred as Delhi–Kolkata Road) is a busy National Highway where traffic density is about 10^6 and Sikandarpur is a small village situated towards the north of Agra city about 3 km from NH-19 and NH-44 and nearly 15 km away from the industrial sectors of the city.

Agra is located in the north central (27°10' N, 78°05' E) part of India which is about 200 km southeast of Delhi and lies in the middle of the Indo-Gangetic Plain. Climatically, Agra is hot and dry during the summer and cool in the winter. The annual rainfall is about 650 mm with 90% being received during monsoon season (July–September).Winter is associated with calm periods while during the summer and monsoon strong surface winds are observed. Maximum and minimum temperatures in summer are normally 45°C and 25°C, respectively, while in the winter it ranges between 3°C to 10°C. Relative humidity is highly variable from 25–99%. Apart from the local sources Mathura refinery and Firozabad glass industries are both situated at a distance of 40 km from Agra. National Highway lies about 2 km from the sampling site. Although there are no industries in the immediate vicinity of the sampling site, during the monsoon, site becomes downwind with respect to the city's pollution sources.

SAMPLING AND ANALYSIS

O_3 AND NO_X MEASUREMENT: Surface O_3 and NOx concentration will be recorded using continuously operating O_3 analyzer (Thermo Fischer Model 49i) and NOx analyzer (Thermo Fischer Model 42i). The ozone concentration measurement is based on ultraviolet absorption photometry; the principle is that ozone (O_3) molecules absorb UV light at a wavelength of 253.7 nm. The absorption of UV-light by O_3 molecule is directly related to the ozone concentration (Beer-Lambert law). Calibration of the system is done with the help of a built-in ozone generator and zero air generator. There is an ozone scrubber which removes ozone from the air supplied by a zero air generator and it

acts as a reference. The sample is drawn through the sample bulkhead and is split into two gas streams. One gas stream acts as reference gas, flows to the reference solenoid valve. Other stream i.e. the sample gas, flows directly to the sample solenoid valve. The solenoid valves alternate every 10 seconds. The NO_X analyzer operates on the principle that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. An infrared light emission occurs when electronically excited NO_2 molecules reaches its ground state. NO_2 is converted to NO by molybdenum NO_2 to NO converter. Molybdenum has ~100% conversion efficiency. The detection limit of O_3 and NOx analyzer is 0.5 ppb and less than 50 ppt respectively.

CO MEASUREMENT: Surface CO will be recorded using continuously operating CO analyzer (Model T300). The analyzer works on the principle, Beer-Lambert Law by absorbing an IR radiation at 4.67 μm (vibration-rotation band of CO). The T300 uses a high-energy heated element to generate a beam of broad-band IR light with known intensity. This beam is directed through multi-pass cell filled with sample gas. The sample cell uses mirrors at each end to reflect the IR beam back and forth through the sample gas a number of times. The total length that the reflected light travels is directly related to the intended sensitivity of the instrument. Finally, the beam strikes a solid-state photo-detector that converts the light signal into a modulated voltage signal representing the attenuated intensity of the beam. The detection limit of analyzer is 0.04 ppm.

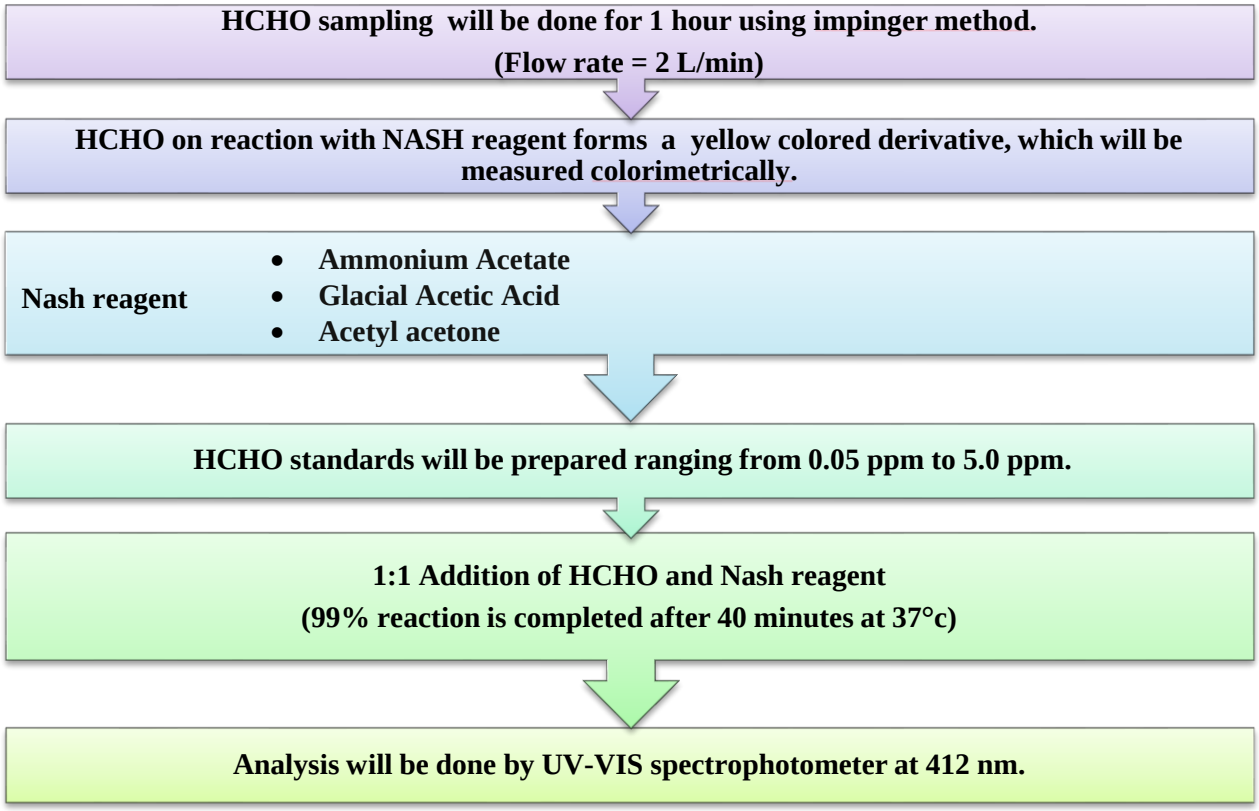
CALIBRATION: Zero air generator and dynamic gas calibrator (Teledyne model, T700) will be used for weekly zero and monthly span calibration of the analyzers by NIST standards.

METEOROLOGICAL PARAMETERS: Automatic Weather Station WM271 Data Logger at sampling sites will be used for recording meteorological parameters viz. wind speed, wind-direction, relative humidity, temperature and solar radiation at 1-h interval.

VOCs: Sampling will be carried out by active grab sampling method at all the three sites. A battery operated portable sampling pump (SKC 224-XR) will be used to draw air at the rate of 0.1 ml min^{-1} for 1 hour through SKC adsorption cartridge containing activated charcoal (60–80 mesh). The sampling pump will be calibrated by an electronic digital flow calibrator. Six samples per day will be collected to diurnal studies. The sample tubes will be placed in polythene bags that seal tightly and kept in a box in a deep freezer until analysis. Extraction of samples will be done in CS_2. Analysis will

be done by Agilent 5977B Gas Chromatography Mass Selective Detector/Flame Ionization Detector (GC-MSD/FID, Agilent Technologies, USA). Analyses will be performed by injecting 1 µL of extract in injector (250 °C) in a split mode, (split ratio will be 27:1 and split flow will be 32.4 mL/min). Sample will be first separated by a DB-17MS capillary column (30 m length × 0.25 mm internal diameter × 1.25 µm film, Agilent Technologies, USA), with helium as the carrier gas at a constant rate of 5.0 mL/min, and to a HP-5MS column (30 m length ×0.25 mm internal diameter × 1.25 µm film, Agilent Technologies, USA) output to flame ionization detector (FID) detection. The GC oven temperature will be programmed to be initially at 50 °C, held for 3 min; then increased to 140 °C at 10 °C/min, and then to 240 °C at 20 °C/min with a final hold time of 19 min. The MSD will be operated in selected scan monitoring mode.

HCHO


HCHO sampling will be done for 1 hour using impinger method.
(Flow rate = 2 L/min)
HCHO on reaction with NASH reagent forms a yellow colored derivative, which will be measured colorimetrically.
Nash reagent
Ammonium Acetate
Glacial Acetic Acid
Acetyl acetone
HCHO standards will be prepared ranging from 0.05 ppm to 5.0 ppm.
1:1 Addition of HCHO and Nash reagent
(99% reaction is completed after 40 minutes at 37°c)
Analysis will be done by UV-VIS spectrophotometer at 412 nm.

HEALTH RISK ASSESSMENT

Benzene exhibits cancer risk while toluene, ethylbenzene and xylene possess non-carcinogenic effects in the term of hazard quotient (HQ). Using the Integrated Risk Information Systems of USEPA 1997,

the exposure assessment parameters such as lifetime cancer risk (LCR) and hazard quotient (HQ) have been calculated using the following equations:

$$LCR = CDI \times SF \quad (1)$$

$$HQ = CDI/RfD \quad (2)$$

Where CDI, SF, and RfD represent the chronic daily intake (mg/ kg/day), slope factor $(mg/kg/day)^{-1}$, and reference dose (mg/kg/ day) of the chemical. HQ denotes the non-cancer health hazard by individual chemical while hazard index (HI) represents the total non-cancer health hazard by all targeted chemicals. Equation (3) has been used to evaluate the CDI of each compound:

$$CDI = \frac{CA \times IR \times ET \times EF \times ED}{BW \times AT \times 1000} \quad (3)$$

Where CA is the VOC concentration ($\mu g/m^3$), IR is an inhalation rate (m^3/h), ET is the exposure time (h/day), EF is exposure frequency (day/year), ED is the exposure duration (year), BW is a body weight (kg), AT is averaging time (year), and 1000 is the conversion factor (μg/mg). For CDI calculation, Inhalation rates of 0.83 and 0.87 m^3/h while body weights of 70 and 36 kg for adults and children were used, respectively. Other parameters such as ET, EF, ED, and AT were assumed to be 24 h/day, 350 d/year, 30 years and 70 years, respectively.

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